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PHYSICAL PARAMETERS IN SYNTHOIL PROCESS

Quarterly Report for the Period
July–September 1975

by

J. Fischer, R. Lo, S. Nandi,
D. Fredrickson, T. Bump,
T. Mulcahey, H. Huang, and A. Jonke

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Available from
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Price: Printed Copy \$4.50; Microfiche \$2.25

ANL-75-76

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

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J. Fischer, R. Lo, S. Nandi,*
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and A. Jonke

Chemical Engineering Division

December 1975

* Chemistry Division

** Components Technology Division

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ABSTRACT

This work is being done in support of the development of processes for converting coal to liquid fuel of low sulfur content, suitable for use in power production. Most of the effort is intended to produce information applicable to the SYNTHOIL Process.

In the SYNTHOIL Process for converting coal to a low-sulfur fuel oil, coal is liquefied and hydrodesulfurized in a turbulent-flow, catalytic packed-bed reactor. A slurry of coal in recycled oil is reacted with hydrogen at 450°C and 2,000-4,000 psi in the presence of Co-Mo/SiO₂-Al₂O₃ catalyst. The turbulent flow of fluid prevents the coal's mineral matter from settling and plugging the reactor. The gross liquid products are centrifuged to remove the unreacted solids. The centrifuged liquid product is a low-sulfur, low-ash fuel.

The work for this program includes four tasks now in the planning stage of development.

Task I, Heat of Reaction of Hydrogen with Coal Slurries. Determination of the heat of reaction of coal slurry with hydrogen, with and without catalysts, in the ranges, 2,000-4,000 psi and 400-475°C.

Task II, Heat Transfer Coefficient. Determination of coefficient of heat transfer from SYNTHOIL reactor fluids to heat exchangers in the following range of conditions: pressure, 2000-4000 psi, temperature, to 475°C.

Task III, Additives to Facilitate Separation of Solids from Liquids. Investigation of additives to facilitate solids removal, evaluation of the effect of commercially available additives on the separation of solids from the liquid products by centrifugation and filtration, and evaluation of five commercially available additives for reducing the viscosity of the product oil. Determination of the temperature coefficient of viscosity for the two most promising combinations of the additives and product oil.

Task IV, Catalyst Testing. Screening of new catalysts in 300-hr runs in a continuous high-pressure coal liquefaction unit to operate at 2000-4000 psi at a minimum feed rate of 4 oz per hr. of coal slurry containing 35-50% coal. The product samples will be collected and analyzed for coal conversion; sulfur, nitrogen, and oxygen removal; hydrogen consumption; viscosity; and specific gravity.

SUMMARY

Heat of Reaction of Hydrogen with Coal Slurries
(S. Nandi and D. Fredrickson)

Heat of reaction data will be obtained for the hydrogenation of coal slurries typical of those used in the SYNTHOIL process. In this process, a coal-in-oil slurry is converted to fuel oil by catalytic hydrogenation. The chemical reaction is exothermic, and a knowledge of the amount of heat released in the process preheater and in the reactor is necessary for process design. Experimental data is not available.

Experimental equipment is being designed for this work. A calorimeter will be required which will allow study of the heat of reaction of hydrogen with coal slurries at 2000 to 4000 psi and at 400 to 475°C.

Heat Transfer Coefficient
(T. Mulcahey and T. Bump)

Work on this program was initiated in September 1975 to provide measured heat transfer coefficients from the SYNTHOIL Process feed and effluent products, to container walls. These data will be used in future design of heat transfer equipment for the SYNTHOIL Process. Initial efforts are directed at obtaining preliminary design information for sizing and ordering long-lead procurement items needed for construction and operation of a heat transfer coefficient measurement unit. A detailed unit design to accommodate the ranges of temperature, pressure, fluid flow, and fluid consistency involved in the SYNTHOIL heat transfer process will be developed later. The location for construction of the unit has been tentatively selected, and a review of the site modifications has been initiated.

The Pittsburgh Energy Research Center (PERC) was visited to obtain information related to SYNTHOIL Process unit operation, to establish the experimental unit size, and to determine which items may take a long time to procure. Sufficient information was obtained to permit initiating both vendor and preliminary design discussions. The slurry and hydrogen flow rates will be comparable to those of the 1/2-ton-per-day PERC facility.

A preliminary review of available literature was performed. This, plus a preliminary review of the SYNTHOIL facilities and process development, indicates that there are many problems (discussed in Section II of this report) attendant with obtaining meaningful heat transfer coefficients for design of SYNTHOIL Process heat transfer equipment. Definition of some of these problems; assessment of the influence these problems may have on the measured heat transfer coefficients, facility design, and operation; and test section design have been initiated.

Additives to Facilitate Separation of Solids from Liquids.
(H. Huang)

Product effluent from the SYNTHOIL or CO-STEAM coal liquefaction processes currently being developed by the Pittsburgh Energy Research Center must be reduced in solid content before it is suitable for use as a fuel in power

production facilities. Two methods of solids removal, centrifugation and filtration, are now being investigated at PERC. Neither removal technique results in sufficient solid removal. Water emulsion formation and frothing due to the high water content of lignite used in the CO-STEAM process also complicate solids removal in this process.

The objective of this task is to investigate the effect of suitable additives in facilitating the removal of solids from oil produced in coal liquefaction processes. A number of commercially available surfactants and viscosity-changing agents will be evaluated as additives to the product effluent from coal liquefaction processes. These additives should be able to act either as agglomerating or flocculating agents and should alter the physical properties of the mixture, improving the subsequent separation steps. The ideal additives should reduce the viscosity of the product, modify the interfacial tension of the phases, depress the pour point, and induce flocculation of the solid particles.

Catalyst Testing

(R. Lo)

The objective of this task is to evaluate new commercially available catalysts for use in the SYNTHOIL process. A continuous high-pressure coal liquefaction unit will be designed and constructed to operate at SYNTHOIL process conditions-- 450°C and 2000 to 4000 psi. Catalysts will be tested in 300-hr continuous runs. The evaluation will be made on the basis of analyses of coal input and product samples. Samples collected at least once every 24 hr will be analyzed to obtain information on percent coal conversion; sulfur, nitrogen, and oxygen removal; hydrogen consumption; oil viscosity; and specific gravity.

The bench-scale unit used at PERC is very similar to the one we will be using. A work project for this task has been established. Initial contacts have been made with equipment vendors and manufacturers in order to obtain information for use in the construction of the catalyst test unit.

I. HEAT OF REACTION OF HYDROGEN WITH COAL SLURRIES (S. Nandi and D. Fredrickson)

Heat-of-reaction data will be obtained for the hydrogenation of coal slurries typical of those used in the SYNTHOIL process. In this process, a coal-in-oil slurry is converted to fuel oil by catalytic hydrogenation. The chemical reaction is exothermic, and a knowledge of the amount of heat released in the process preheater and in the reactor is necessary for process design. Experimental data is not available.

Experimental equipment is being designed for this work. A calorimeter will be required which will allow study of the heat of reaction of hydrogen with coal slurries at 2000 to 4000 psi and at 400 to 475°C.

Takeya *et al.*¹ hydrogenated coal in process-derived oil and reported a value of 400-460 cal/g of coal converted. The conditions of their experiment were different from that of the SYNTHOIL process, but this value serves as a guide for experimental design. Lee *et al.*² determined the heat of hydrogasification of coal and chars at 700-815°C and 1000 psi (68 atm). The heat liberated at 810°C and 1000 psia (68 atm) using raw Ireland Mine Coal (C = 81 % daf) was found to be in the range 861 to 1022 cal/g of coal reacted. The amount of coal reacted was determined from the ash enrichment of the solid residue remaining after an experiment. In principle, if the ultimate analyses of the reactants and products are known along with the mass balance, it is possible to convert the experimental heat measured per unit weight of coal to a value based on the amount of hydrogen consumed in the reaction, which is the value required for process design.

Akhtar,³ drawing an analogy from the hydrogenation of petroleum fractions, suggests that the heat of coal liquefaction may be in the range 5500 to 11000 cal/g of hydrogen consumed.

It is the objective of this detail to obtain the heat of hydrogenation of coal under SYNTHOIL process conditions. The heat release data is required for proper design of the slurry preheater and the reactor of the SYNTHOIL plant. Two procedures for obtaining the heat of hydrogenation data may be considered, an indirect method and a direct method.

A. Indirect Method

One approach is to use heat balance data that can be obtained from a SYNTHOIL Catalyst Test Reactor. The heat of reaction (hydrogenation) can be calculated from the heat of combustion of the reactants and products. The heat of combustion can be obtained with a Parr bomb calorimeter or calculated with a modified Delong formula if the elemental analyses are available. The accuracy of the calculated heat is dependent on the accuracy of the material balances. Another drawback of the procedure is that the calculated heat of reaction at 25°C is determined, no information being obtained on the reaction heat at the actual reaction temperature.

A new method of predicting heat release in hydrogenation of petroleum hydrocarbon feed stock has been described in a recent publication.⁴ Typical petroleum reactions in which hydrogen is consumed have been classified

according to the quantity of heat released: olefin saturation, 27-30 kcal mol⁻¹ of H₂; aromatic saturation, 14.5-16.5 kcal mol⁻¹ of H₂; and saturate cracking, 7-10 kcal mol⁻¹ of H₂. To use such an approach, we would need accurate mass spectral analyses of reactants and products.

B. Direct Method

1. Determination of Heat of Hydrogenation by Differential Scanning Calorimetry

Mahajan *et al.*⁵ obtained the values of integral heat of hydrogenation of dry coal up to a temperature of 570°C and 55 atm of hydrogen using a commercial differential scanning calorimeter. Milligram quantities (20 mg) of samples were used, and the extent of reaction was obtained from weight losses. In principle, coal slurries could be used in this kind of experimental setup. The pressure range of the experimental system could be increased by suitable modifications. The main drawback of this approach is that the products of the reaction can not be determined accurately because of the small sample size and therefore the heat released can not be expressed on the basis of hydrogen consumed in the reaction.

2. Calorimetry in a Batch-type Autoclave

A reaction calorimeter has been used by Lee *et al.*² This autoclave-calorimeter, in which 15-g coal samples can be used, was designed to measure the heat released for the reaction



Liquid samples or slurries can be used in place of dry coal. A vacuum heat shield surrounds the main autoclave, and a number of sensors are attached to the outside walls of the autoclave. As a result of these mechanical features, quantitative recovery of the reaction products after hydrogenation is rather difficult and the material balance is poor.

Weller *et al.*,⁶ working with a batch autoclave, reported a good material balance for coal hydrogenation. The purpose of their study was to investigate the kinetics of coal liquefaction. Consequently, the system was not intended to measure the heat liberated in the process.

C. Proposed Experimental System for the Measurement of Heat Liberated in the SYNTHOIL Process

Reaction calorimetry consists essentially of two parts: (1) measurement of the heat liberated in the process and (2) estimation of the extent of reaction. The apparatus of Lee *et al.*² meets the first requirement, but the extent of reaction can not be measured with the required accuracy. Therefore, it is proposed to incorporate some features of the product analysis methods used by Weller⁶ in the reaction calorimeter of Lee *et al.*,²

A batch high-pressure, high-temperature calorimeter is being considered for use in this work.

D. Schedule of Deliverables

- a) The apparatus for determination of the heat of reaction will be constructed and installed by March, 1976.
- b) The heat of reaction of slurry and hydrogen with catalyst absent will be delivered by June, 1976, for the operating conditions, 400-475°C and 2000 psi.
- c) The heat of reaction with catalyst absent for the operating conditions, 400-475°C and 4000 psi, will be delivered by September, 1976.
- d) The heat of reaction in the presence of catalyst over the full operating range (400-475°C, 2000-4000 psi) will be delivered by June, 1977.

II. HEAT TRANSFER COEFFICIENT (T. Mulcahey and T. Bump)

The objectives of this task are to determine heat transfer coefficients applicable to the SYNTHOIL Process feed heat exchangers and effluent heat exchangers and to identify mechanisms for the heat transfer process. Information will be supplied, in a form suitable for SYNTHOIL heat exchanger design, on heat transfer film coefficients for (a) SYNTHOIL reactor effluent cooled by a metal surface and (b) SYNTHOIL feed heated by a metal surface. The following ranges of conditions will be covered:

Pressure:	2,000-4,000 psig
Temperature:	200-475°C
Flow of Fluids:	Turbulent

The experimental work will be carried out in a 1/2-ton-per-day heat transfer test loop which will include a slurry tank, feed pump, heater, cooler, let-down tanks, and power, flowrate, and temperature instrumentation. Three different coals suitable for SYNTHOIL processing will be studied in the investigation. Theoretical modeling of the heat transfer process will be attempted, correlating primary interaction of the liquid, particles, and walls. The resulting model should be capable of describing the net transfer rates, as well as the temperature history, of the particles in the slurry.

Initial efforts have been directed at obtaining information about the design for and items required for construction and operation of a heat transfer coefficient measurement unit. First consideration will be given to the purchase of items that will require long delivery times. A successful visit was made to the Pittsburgh Energy Research Center (PERC) to review the SYNTHOIL Process facilities there and to obtain information related to facility operation and design, past experience, and future plans for the SYNTHOIL Program, of which this task is a part. Recommendations by PERC personnel indicated that the slurry pump and hydrogen compressors would be

the long lead items and that these items are of such a general nature that their capabilities, if sized for the maximum needed flow rates, would be sufficient to handle all conditions. Contact was initiated with the recommended vendors. As a result of the information obtained during the trip, the ANL SYNTHOIL heat transfer coefficient measurement unit has been sized to have a slurry feed rate of about 25 lb/hr and with a hydrogen circulation rate of 1300 scf/hr comparable to that used in a SYNTHOIL Process of 1/2-ton-per-day facility. A tentative location for the ANL unit has been selected in Building 205 (which houses the Chemical Engineering Division), and a review of the site modifications necessary to accommodate the unit has been initiated. Adequate utilities, including electricity, water, drainage, steam, and barriers, are present; utility availability will be confirmed when more detailed information on the needed power, cooling, and air circulation becomes available.

A preliminary review of the available literature, coupled with the review of the SYNTHOIL facilities and process development, indicates that many problems exist in obtaining meaningful heat transfer coefficients for design of SYNTHOIL process heat transfer equipment. Definition and assessment have been initiated on the effects of these problem areas in the design, construction, operation, and maintenance of a heat transfer test unit. A preliminary discussion of some of these problem areas follows:

1. Chemical reactions, with unknown amounts of heat release, occur during preheat of the slurry-hydrogen mixture; these chemical reactions introduce an internal heat generation term into the heat balance and heat transfer equations. This unknown value of the heat generation term may introduce an error into the measurement of the heat transfer coefficient.

2. Slurry constituents dissolve and/or vaporize or condense during preheat or effluent cooling at unknown rates and release or absorb unknown amounts of energy.

The solution to the above problems involves an assessment of the desirability of separating the chemical or phase change effects from the heat transfer process since they are an inherent part of the SYNTHOIL process and would have to be accounted for anyway. Also, making an experimental determination of some of the chemical effects may be possible by obtaining data using inert gas instead of hydrogen. An inert gas will probably be used in some experiments to minimize chemical reactions.

3. Usually, heat transfer coefficients are correlated using dimensionless numbers which involve material properties that vary slowly. The slurry preheat process in the presence of hydrogen involves mixed phases (gas, liquid, and solid), which do not have well-behaved characteristics.

Volumetric changes in the coal, coupled with severe viscosity changes and presumably similar changes in specific heat, thermal conductivity, and amounts of each phase, will create problems in correlating or extrapolating results. Currently, it is assumed that a hydrogen Reynolds number of 10,000, based on a duct empty of either slurry or packing, is sufficient to produce the turbulent flow conditions desired for the experiments. However, further developments could modify this assumption.

4. The geometry and size of the preheat and cooling equipment and the relative volumetric flowrates of gas and liquid/solid phases in the SYNTHOIL process may introduce geometrical-effects problems with regard to correlation and application of results.

Under some conditions, heat transfer is known to be affected by geometrical considerations, *e.g.*, horizontal *vs.* vertical tube or plate condensation. These effects may be even more pronounced when large amounts of noncondensable gases are present or when a mist of liquid is entrained within the gas, as in the effluent cooler.

5. No problem is expected regarding the availability of coal of the proper mesh; however, there is always the problem of ensuring that a small sample of coal is representative of the overall mine output. A sufficient amount of each of the three coals will be obtained to ensure an adequate supply for the duration of the experiments involving each of the three coals and to try to ensure consistency of results by maintaining uniform samples.

Availability of SYNTHOIL products poses a problem; only a limited amount of the refined and unrefined liquid will be available. It may then be necessary to substitute more readily available materials for initial experiments. Manufacture or simulation of effluent gas for use in the experiments may be necessary. Incomplete data on the SYNTHOIL Process effluent composition may limit the ability to produce exactly representative experimental conditions.

6. The experimental facility, as currently envisioned, consists of a preheater section of about 1/4-in. ID to ensure turbulent flow in an unpacked tube. The use of expansion volumes in such an experiment to insert instruments needed for temperature, flow, and pressure determination may create local problems of settling, stratification, and temperature and pressure changes (due to gas expansion or velocity changes). A balance will be made between errors introduced by incorporation of measurement instrumentation and disturbances into the system, and errors due to insufficient instrumentation.

Schedule of Deliverables

- a) The test loop for measuring heat transfer film coefficients will be constructed and installed by June, 1976.
- b) Film coefficients for cooled effluent will be delivered by December, 1976.
- c) Film coefficients for heated feed will be delivered by June, 1977.

III. ADDITIVES FOR SEPARATION OF SOLIDS FROM LIQUIDS (H. Huang)

The objective of this task is to investigate the use of suitable additives to facilitate the removal of solids and oil produced in coal liquefaction processes. A number of economically practical, commercially available surfactant or conditioning agents will be added to the product effluents from

coal liquefaction processes, such as SYNTHOIL and CO-STEAM. These additives should be able to act either as agglomerating or deemulsifying agents and/or to alter the physical properties of the mixture, so as to improve the separation in subsequent steps. The properties which may be altered and for which experimental data will be collected are viscosity, interfacial tension, and flocculation characteristics. This information will be useful in the design of schemes for the separation of solids from liquids in coal liquefaction processes.

In this report, we first present background information on the separation techniques now under development at PERC (Pittsburgh Energy Research Center) and additive treatment of the product, and then outline the proposed experimental program.

The product effluent from the hydrodesulfurization reactor in the SYNTHOIL process typically contains 6 to 8 wt % ash, 2 to 6 wt % benzene insolubles, and the mineral matter originally present in the coal. For the CO-STEAM process, the product consists of about 7 to 10 wt % water, 5 to 8 wt % benzene insolubles, with the remainder made up of oil and gas. As specified by a major supplier of gas turbines, the maximum permissible concentration of ash in liquid fuel is 0.005 wt %. Therefore, further removal of solid residues is necessary in order to upgrade the quality of the product oil.

Two methods of solids removal are now being investigated at PERC: centrifugation and filtration. The centrifugation studies are being conducted with a Sharples Super centrifuge, which has a 4-in. ID x 30-in. long vertically placed bowl operated at 15,000 rpm. Thirty minutes of centrifugation time is allowed for each 90- to 95-lb batch. All centrifugations are conducted at 80°C.

Table 1. Centrifugation of the Whole Product Oil from Kentucky Coal⁷

<u>Process Variables</u>				
Pressure, psi.	4,000	4,000	2,000	
Preheater temperature °C	450	430	430	
Residues, wt % of whole product. .	11.7	12.1	12.1	
S in residues, wt %.	4.6	5.2	4.9	
<u>Solvent Analysis of Residues, Wt %</u>				
Ash.	52.8	53.0	55.3	
Organic benzene insolubles	14.9	14.1	17.5	
Asphaltenes	3.1	5.6	6.5	
Oil.	29.2	27.3	20.7	
Centrifuged liquids, wt % of whole product	88.3	87.9	87.9	
S in centrifuged liquids, wt %. . . .	0.2	0.45	0.6	
<u>Solvent Analysis of Centrifuged Liquids, wt %</u>				
Ash.	0.1	0.75	2.1	
Organic benzene insolubles	0.8	0.9	4.4	
Asphaltenes.	10.8	18.7	27.6	
Oil.	88.3	79.65	65.9	

Table 1 reveals the effectiveness of centrifugation. On the average, the centrifuge residues constitute about 12% of the whole product and contain about 55% ash and 14 to 18% benzene insolubles. Comparison of these figures with the concentration of the corresponding components in the centrifuged liquids indicates that centrifugal removal of ash and benzene insolubles is very effective for the product at 4,000 psi and 450°C. However, the ash content of the liquid produced at 2,000 psi and 430°C and centrifuged results in a liquid of too high a viscosity.

Both batch filtration and continuous rotary drum filtration are being conducted at PERC. Batch tests, using 1 μ m porosity Polypropylene cloth as the medium, give clear evidence that filtration through cloth media has the potential for de-ashing coal-derived oil to a fuel suitable for firing in a gas turbine. A sample of filtered oil taken after 3 hr contained 0.009% ash, and a sample taken after 4.3 hr contained only 0.002% ash, although the filtration rate of 9 lb ft⁻² hr⁻¹ is relatively low. The operating conditions were 80°C and 185 psi. Work with the continuous rotary drum filter is at a more preliminary stage, and no information is available.

The above description of centrifugation and filtration deals principally with product from the SYNTHOIL process. Another problem has been identified in removing solids from the CO-STEAM product. The higher water content of lignite used in the CO-STEAM processes results in a water-in-oil emulsion which makes centrifugation and filtration difficult. Emulsion breaking becomes necessary to increase the efficiency of those separation steps.

It has long been recognized that treatment by both chemical and physical means makes solid-liquid separation more efficient.⁸⁻¹¹ Chemical treatment, with aging, produces flocculation and/or coagulation. Physical pretreatment, on the other hand, which consists of crystallization, temperature adjustment, freezing, and the introduction of admixed material, modifies slurry properties, particularly viscosity and interfacial tension between the liquids and individual solid particles. In this study, we will be mainly concerned with physical property modification and flocculation.

A. Viscosity Reduction

The instantaneous flow rate of liquid through a batch filter is inversely proportional to the liquid viscosity. With a cyclic filter, such as the rotary drum type used by PERC, it can be shown that the average rate of flow is inversely proportional to the square root of the viscosity. In centrifugation, according to Stokes' law, the terminal settling rate of a particle is inversely proportional to the viscosity of the liquid.

From the above brief statements, it is clear that there is good reason to endeavor to reduce the viscosity of a liquid to facilitate separation. In practice, two important techniques are available, (a) raising the temperature, and (b) dilution with a less viscous liquid. Raising the temperature, an old concept, is still very important, both because it is generally simple and convenient, and also because a large reduction in viscosity can often result from a small increase in temperature, particularly with highly viscous liquids.

Dilution with a less viscous liquid additive is also a valuable technique, although it is inevitably limited in application since it increases the volume to be filtered and may also require further processing of the filtrate such as distillation. Accordingly, considerable care may be required in selecting the optimum economic degree of dilution. Universal Oil Product (UOP) is currently studying this problem.

B. Interfacial Tension

Two types of interfacial tension are involved in this study: solid-liquid interaction and liquid-liquid interaction.¹²⁻¹⁴ The surface conditions at the point where liquid and solid come in contact critically influence the amount of residual liquid absorbed on the solids, both in sedimentation and cake filtration. Surface-active agents can be very useful in reducing the ability of a liquid to wet a solid and hence in minimizing the residual liquid contained in the recovered solids.

Both liquid-liquid and liquid-solid interactions appear to be involved in the emulsion problem which has been experienced in the separation of the CO-STEAM product. Emulsification is a complicated phenomenon and is not yet fully understood. It has been postulated that the tiny dispersed liquid droplets possibly carry small charges of the same sign and that this prevents coalescence. Also, suspended solids, such as benzene insolubles, may act as emulsifying agents.

Deemulsification has been employed in the petroleum industry. Electrical, mechanical, and chemical methods all have been employed for this purpose. The generally accepted theories of additive deemulsification have held that an added chemical may break an emulsion by one of the following mechanisms: (a) by reacting with the emulsifier to give a precipitate or a product soluble in one of the phases, (b) by tending to form an emulsion opposite in type to that to be broken, (c) by neutralization of electrical charges in the dispersed droplets.

C. Flow Improvement¹⁵

For a potential coal liquefaction process to have commercial possibilities, the product oil should be capable of being used as a recycle vehicle oil for preparing pumpable coal-oil slurries. PERC personnel have observed that with certain kinds of coal, the product oil is too heavy to serve as a transportation oil. This problem has also been recognized in the petroleum industry, and various additives have been suggested for depressing the pour point of the fuel oil. It is believed that these pour depressants function not only by retarding wax crystal growth but also by destroying cohesive forces between the crystals.

D. Flocculation

Flocculation is a process whereby individual particles are united into rather loosely bound agglomerates, or flocs, thereby increasing the effective particle size of solids suspended in a liquid. The degree of flocculation is controlled by the probability of collision between the particles and the tendency toward adhesion after collision. The probability of collision can be increased by agitation, while the adhesion tendency can be increased by adding agents commonly known as flocculants.

Agents act as flocculants by one or more of three general mechanisms: (a) Neutralization of the electrical repulsive forces surrounding the small particles, which enables the van der Waals' cohesive force to hold the particles together once they have collided; (b) Precipitation of flocs; (c) Bridging of particles by natural or synthetic long-chain, high-molecular-weight polymers. Choice of flocculants is often limited by incompatibility with the process. The normal procedure is to choose agents or combinations of agents most likely to be effective and to test them in various quantities. An ideal additive should be able to simultaneously perform the above four functions well.

E. Experimental Program

Planned experiments to evaluate the effect of commercially available additives on the viscosity, interfacial tension, and flocculation characteristics of liquefaction product oil are described below:

1. Viscosity Measurement¹⁶

Viscosity measurement is simple for normal Newtonian fluids. The coal-derived oils, however, tend to change with time and behave like time-dependent non-Newtonian fluid, possibly due to autoxidation. Some effort will therefore be spent to either determine the effect of aging on viscosity or to use some technique to prevent the investigated fluid from being exposed to air. A rotational type viscometer will be used for this work.

2. Interfacial Tension

Tensiometers are commercially available for measurement of interfacial tension between two liquid phases. To simulate the real situation, however, the "oil" used in the investigation should be capable of representing the real "product oil." This demands that either the product oil, after separation steps, be directly used or that the composition of the product oil be known accurately so that it can be simulated. Determination of interfacial tension between liquid and solid for our system will be complicated since the suspended solid particles are irregular both in size and shape. We may need to characterize the particles first. Particle analysis and characterization are frequently overlooked as efficient design tools by the nonspecialist.⁸

3. Flocculation Test

Qualitative evaluation of flocculants is easy to perform, but accurate quantitative correlation is generally hard to obtain. A number of methods have been suggested in Ref. 8. These include sedimentation tests by rate of settling and turbidity measurements. The method or combination of methods which will be employed in this study will be specified at a later date.

F. Scope of Work

The effect on the physical properties of coal liquefaction products with the addition of commercially available additives will be determined. The properties for which data will be delivered for coal liquefaction products are viscosity, interfacial tension, and fluoccculation characteristics.

Temperature coefficients of viscosity will be supplied at intervals of 50° from 25 to 250°C for the two most promising combinations of additives and product oil.

G. Schedule of Deliverables

Viscosimetry equipment and the commercial additives to be studied will be obtained by December 1975. By July, 1976, the viscosity and temperature coefficient determination will be completed.

IV. CATALYSTS TESTING (R. Lo)

In the SYNTHOIL process for converting coal to a low-sulfur fuel oil, coal slurried in recycle oil is transported by a high-velocity, turbulent flow of hydrogen through a reactor containing a fixed bed of catalyst. The development so far has been with a pelletized commercial Co-Mo catalyst (Harshaw 0402T). Screening of other catalysts in short-term batch autoclave tests has been conducted to determine their initial activity,¹⁷ but no tests have been made in longer runs in a continuous unit simulating the conditions of SYNTHOIL. There is a pressing need to determine the effectiveness of these catalysts beyond the initial activity that they exhibited. This information will assist in the choice of a catalyst to be used in the SYNTHOIL pilot plant.

The objective of this task is to evaluate new commercially available catalysts for use in the SYNTHOIL process. This test will be carried out in a continuous unit under the operating conditions of SYNTHOIL. Results gained from this study will be used to identify the better catalysts. Subsequent screening of these selected catalysts will then be made on the long-life test unit at PERC to optimize catalyst selection for use in a 10 ton per day SYNTHOIL process development unit currently under design.

This work will be performed in two phases.

A. Phase I. Design, Construction and Shake-down of Test Unit

We will design (consulting with PERC) and construct a continuous high-pressure coal liquefaction unit wherein catalyst may be tested under SYNTHOIL process conditions, 450°C and 2000-4000 psi. The unit shall have the capacity to process at least 4 oz/hr of coal slurry containing 35-50 percent coal in recycle oil. The design will include sufficient instrumentation and will be automated so that it can be operated continuously with minimal attention for periods of no less than 12 days.

B. Phase II. Test of Catalysts

We will select four or more commercially available hydrodesulfurization catalysts, as agreed upon with PERC. We will test them on the catalyst test unit in 300-hr continuous runs to determine the intermediate life and product variability at 2000 psi and 4000 psi for each catalyst. Product samples will be collected at least once every 24 hr during the run and will be analyzed to determine: coal conversion; sulfur, nitrogen, and oxygen removal; hydrogen consumption; viscosity; and specific gravity of the product oil.

C. Description of the Bench Scale Unit at PERC

The catalyst test unit which will be used for our present work is going to be quite similar, both in size and configuration, to a bench-scale unit used at PERC to study the life of catalyst. An engineering drawing of this unit has been obtained. A visit was made to PERC to study the equipment they used. Their unit is essentially a miniature SYNTHOIL pilot plant. It has almost the same features as in the larger scale 1/2-ton-per-day bench scale plant, but has a different reactor design.

The unit consists of sections for coal slurry feed, hydrogen gas feed, reactor, condenser, and liquid product collection. The entire unit is maintained inside two four-sided, 3/8-in.-thick, steel-walled enclosures. A four-sided pyramidal exhaust duct hangs above the enclosure. The air exhausted from the enclosure traverses the approximately one-foot-square duct opening at about 800 cfm. All high-pressure equipment, reactor, gas-liquid separator, etc. are located in one cell, which is kept locked during the experiments. All valves are mounted behind the cell wall and are manipulated via extension rods.

The coal slurry tank is a cylindrical vessel with a truncated conical bottom directly connected to the slurry transfer pipe. The slurry tank is fitted with a split-type lid so that coal slurry can be introduced periodically during the run. A constant nitrogen stream is directed into the tank to prevent slurry degradation. The slurry tank and attached transfer pipe are supported by an I-beam frame built onto the platform of a Howe-Richardson scale. The coal slurry is continuously circulated in a closed loop by a screw-type Moyno pump. Circulation is maintained to prevent settling of solid coal particles.

A Milton-Roy two-headed slurry pump is used to pump the slurry into the reactor. The pump is a 1/4-in.-piston pump that can deliver 1/2 to 1 quart per hour at a maximum discharge pressure of 4000 psig.

The input gas, mostly hydrogen, is passed through the system at about $40 \text{ ft}^3 \text{ hr}^{-1}$. About $32 \text{ ft}^3 \text{ hr}^{-1}$ is recycled back through the system. Hydrogen, from a standard cylinder outside the equipment enclosure, is regulated and delivered to the system at 500-psi pressure. A single-stage, double-ended, AMINCO diaphragm compressor with a maximum discharge pressure of 10,000 psi is used to bring the hydrogen to the system pressure. A variable-stroke Whitey diaphragm compressor is used to recycle gas.

The entire slurry transfer line from the slurry tank to the preheater inlet, and from the reactor outlet to the low-pressure heavy oil receiver is steam-traced to prevent slurry solidification and plugging. A hydrogen transfer line from the outlet of the back flow check valve to the mixing tee where the gas meets the coal slurry is also steam heated. Electrical heating wire was not used for two reasons: Electric sparks can induce a fire or explosion and coke formation can result at localized hot spots.

The reactor is a 40-ft-long, 1/4-in.-OD x 1/8-in.-ID, 316 S.S. tube, wound into a 4-in.-dia. coil. Catalysts (1/16-in. pellets crushed to pass through 12-14 mesh) was packed into the reactor tube before the tube was

wound into the coiled configuration. The preheater is a 80-ft long, 5/16-in.-OD S.S. tube, wound into a 4-in.-dia coil and joined by welding to the reactor tube. The preheater and the reactor are each enclosed in a three-zone split furnace. Each furnace is rated at 3 kW. Clamp-on thermocouples, made by the U.S. Bureau of Mines, are attached to the preheater and reactor tube for temperature measurements. The reactor is not reusable due to difficulties in removing the spent catalyst.

Distilled water is injected into the liquid product stream just before it passes through the condenser. A Whitey metering pump is used for this purpose. Water is added to scrub out CO_2 , H_2S , and $(\text{NH}_4)_2\text{S}$ from the product stream. Evidently, $(\text{NH}_4)_2\text{S}$ has a tendency to deposit on the condenser tube wall and to plug up the flow.

Liquid product is flashed out from the high-pressure gas-liquid separator to the low-pressure oil receiver through a pair of tungsten carbide valves. The liquid product is collected and centrifuged to separate the oil from unreacted coal and mineral matter. A Sharples centrifuge is used.

Both high- and low-pressure cutoff switches are provided on the unit. Power to furnaces, compressors, and slurry pump will be cut off whenever the system pressure rises or falls beyond preset ranges. Also spring-loaded pressure release valves are attached at various vital locations.

Coal slurry has a tendency to plug the pressure gauge. Therefore, a special arrangement has been made to connect the pressure gauge to a pig-tailed loop, and inject coal-derived light oil, such as anthracene oil, into the loop as a pressure transfer fluid. A hand pump is used to inject light oil into the loop.

Most valves, fittings, and pressure vessels are Bureau-made items. No hydrogen leak detection devices are used in the cell. Leaks are detected by the loss of pressure upon pressurization of the system. The unit was designed for unattended operation. However, the ash and unreacted coal particles tend to settle and to accumulate at the bottom of the gas-liquid separator, making plugging likely. Therefore, the product is flushed at least once every two hours. The unit is operated on a three-shift-per-day basis with one man working on each shift. The longest run made thus far was of 11 days duration.

Both tail gas and flash gas samples are collected periodically in glass bottles and are analyzed by gas chromatography. The gross liquid product is separated into benzene-insoluble, benzene-soluble, asphaltene, and heavy oil fractions by extraction and adsorption techniques. Ultimate analyses are obtained for the coal slurry feed and product oil viscosity, and the specific gravity of product oil is measured by ASTM standard procedures.

A Work Project (combined design, purchases, and installation) for this task has been established. Initial contact has been made with an engineering firm to evaluate the possibility of having the entire unit built by an outside contractor. The engineering firm will provide a rough estimate of the cost and date of delivery. Information on the key system components (slurry pump, compressor, etc.) has been obtained from equipment manufacturers.

D. Schedule of Deliverables

- a) Obtain engineering drawings of the catalysts test unit at PERC by August 1975.
- b) Design, build, and install a catalyst test unit by July 1976.
- c) Deliver data on four catalysts at approximately two-month intervals from September 1976 to July 1977.

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